



# Prediction of the adsorption capacities for four typical organic pollutants on activated carbons in natural waters



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## ABSTRACT

A new model is developed to predict the competitive adsorption isotherms of atrazine, methyl tertiary butyl ether (MTBE), 2-methylisoborneol (2-MIB) and 2,4,6-trichlorophenol onto activated carbons (ACs) in natural water. Based on the Polanyi-Dubinin (PD) equation, with the limiting pore volume of adsorbent estimated from the pore size distribution data, and the Ideal adsorbed solution theory - equivalent background compound (IAST-EBC) model approximation, the model takes into account both the properties of ACs and the impact of natural organic matters in water. Only one set of isotherm in deionized water and one set in natural water are needed to obtain the parameters for the prediction of adsorption isotherms onto different ACs in natural water. The model was employed for the predictions of adsorption capacities for atrazine, MTBE, 2-MIB and 2,4,6-trichlorophenol onto 14 ACs in 22 synthetic and natural waters reported in 9 references, with errors between 14.9% and 44.5% SDEV only. The results suggest that in the proposed PD-IAST-EBC approach, prediction of adsorption capacity for organic compounds onto different ACs in the same natural water is feasible, if the ACs are thermally activated with known pore size information. The model may provide a simple approach for the prediction of adsorption of organic compounds in natural water, and thus greatly reduces the effort required for water utilities when change of AC is needed.

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## 1. Introduction

Powdered and granular activated carbons (ACs) are commonly used in drinking water treatment for the removal of organic micro-pollutants. It is well known that adsorption capacity of ACs is strongly dependent on the properties of ACs, targeted chemicals, and water matrix. The properties of ACs, including specific surface areas (Tan et al., 2008), pore volume and pore size distribution (PSD) (Pelekani and Snoeyink, 1999, 2000), and surface-chemical nature (Li et al., 2002a) have been observed to affect the adsorption of organic chemicals onto ACs. Chemical properties, including functional groups (Crittenden et al., 1999), hydrogen bonding capability (De Ridder et al., 2010), molecular sizes and/or molecular structures (Bunmahotama et al., 2015) are also the factors that

affect adsorption. The properties of water matrix, such as solution pH, ionic strength, and temperature may also influence the adsorption (Al-Degs et al., 2008). However, for the adsorption of organic micro-pollutants in natural water systems, natural organic matter (NOM) has been considered to be the key factor to affect the adsorption (Hyung and Kim, 2008; Li et al., 2003b; Newcombe et al., 2002b).

NOM is present in natural waters in a wide range of concentrations and is a collection of organic compounds of variable sizes, molecular weights, functionalities and adsorbabilities (Sillanpää, 2014). The existence of NOM can adversely impact the adsorption capacity and adsorption kinetics of micro-pollutants onto adsorbents (Smith and Weber Jr, 1989; Shih et al., 2003). Therefore, the adsorption capacity determined in deionized water system cannot represent that in natural water, since the impact of NOM needs to be considered. As the characteristics of NOM is source water dependent, the impact on the adsorption depends on the water source also (Sillanpää, 2014). Therefore, a model capable of quantitatively predicting the impact of NOM on adsorption capacity

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simply based on certain kind of NOM properties, such as molecular sizes and polarity (Hyung and Kim, 2008), would be very helpful for a better design of adsorption processes.

Attempts have been made to model the impact of NOM on the adsorption of organic compounds in natural water (Hung, 2005). Among the models developed, a combination of equivalent background compound (EBC) with ideal adsorbed solution theory (IAST) has been widely used (Graham et al., 2000; Knappe et al., 1998; Najm et al., 1991; Newcombe et al., 2002b; Yu et al., 2008). In the IAST-EBC model, NOM is considered as a single solute (the EBC), while the targeted compound is considered as the other solute. The adsorption of the two solutes is then modeled together by the IAST. This IAST-EBC model has been employed successfully to simulate a variety of chemicals, including naproxen, carbamazepine, non-ylphenol, atrazine, and 2-methylisoborneol (2-MIB) onto different ACs in natural waters collected in US, Australia, Canada and Taiwan (Hung and Lin, 2006a; b; Hung et al., 2005; Knappe et al., 1998; Newcombe et al., 2002b; Yu et al., 2008; Yu et al., 2016). IAST, developed by Myers and Prausnitz (1965) in 1965, is an extensively used (Walton and Sholl, 2015) thermodynamic basis for easily forecasting multi-component adsorption isotherms from only the pure-component adsorption isotherms at the same temperature. IAST rests upon the hypothesis that the adsorbed species form an ideal mixture, that is a sensible approximation in many systems (Babarao et al., 2007; Bae et al., 2008; Cessford et al., 2012; Hand et al., 1985; Keskin et al., 2008; Krishna et al., 2002; Myers and Prausnitz, 1965; Rother and Fieback, 2013; Yang and Zhong, 2006). Although the EBC-IAST model is able to describe the adsorption capacity for a variety of AC/chemical/source water combinations, the model does not take into account the properties of targeted chemicals and ACs and cannot predict the adsorption capacity for different chemicals onto different ACs. Recently, Bunmahotama et al. (2015) successfully developed a model to predict adsorption isotherms of 40 low-molecular-weight nonpolar organic compounds onto 14 ACs in deionized water system. The model, based on the Polanyi-Dubinin (PD) equation, the PSD data of ACs and the molecular structures of organic chemicals, is able to predict the adsorption capacities for organic chemicals onto ACs merely from the PSD data and the chemical properties. It would be very desirable if the model could be applied for natural water systems.

In this study, a new approach, a combination of PD with the IAST-EBC model, is proposed to simulate and predict the adsorption capacity for organic compounds onto ACs in natural waters. The model is aimed to predict the adsorption capacity for the same natural water systems with capability of extrapolating to other chemicals and ACs. All the model parameters were either obtained from literatures or chemical database and no advanced experiments were required. The model was validated with extensive adsorption data for atrazine, methyl tertiary butyl ether (MTBE), 2-MIB and 2,4,6-trichlorophenol onto 14 different ACs from 9 published reports. This novel approach may provide a simple way for the prediction of adsorption capacities for other ACs and chemicals, and therefore is very useful for water utilities when facing changes in targeted chemicals and ACs.

## 2. Methods

### 2.1. Modeling approach

#### 2.1.1. PD model

The PD equation (Dubinin, 1960) modified by Crittenden et al. (1999) is used in this study, as shown below,

$$W = W_0 \exp \left[ - \left( \frac{\varepsilon}{100N} \right)^n \right] \quad (1)$$

where  $W$  is the volume of solute adsorbed (mL/g),  $W_0$  is the limiting volume of the adsorption space, (mL/g),  $n$  is the exponential constant ( $-$ ),  $N$  is a normalizing factor, 100 is a scaling factor,  $\varepsilon = RT \ln (C_s/C)$  in aqueous system (cal/mol),  $C$  is the aqueous phase concentration (mg/L),  $C_s$  is the aqueous solubility (mg/L),  $R$  is the gas constant (1.987 cal/mol/K), and  $T$  is the absolute temperature (K).

To predict the adsorption capacity,  $W$ , three parameters,  $W_0$ ,  $n$ , and  $N$  need to be determined in advance. Generally,  $W_0$  for a specific AC may be obtained from the regression of isotherm data, as shown by Crittenden et al. (1999). Although precise estimation of  $W_0$  for a specific GAC/chemical system may be obtained through this method, experiments for isotherm data are required. In this study, the method proposed by Urano et al. (1982), and later successfully used by Hung and Lin (2007) and Bunmahotama et al. (2015) is applied. In the method  $W_0$  can be estimated from PSD of ACs, as described in equation (2)

$$W_0 = 0.055 \text{ mL/g} + V_{3.2} \quad (2)$$

where  $V_{3.2}$  is the micropore volume for pores with diameter less than 3.2 nm for AC. For another parameter,  $n$ , that represents the property relevant to the surface heterogeneity, was determined by Bunmahotama et al. (2015) to be 1.1 and this value is used in this study. For the third parameter in the model, the normalizing factor  $N$ , its estimation is based on molecular connectivity indices (MCIs) as also described in Bunmahotama et al. (2015).

#### 2.1.2. IAST-EBC model

The IAST-EBC model, when combined with the Freundlich isotherm ( $q = KC^{1/n}$ ) to describe the single-solute adsorption for both target organic compound and EBC, can be expressed as Najm et al. (1991):

$$C_{1,0} - q_1 C_c - \frac{q_1}{q_1 + q_2} \left( \frac{n_1 q_1 + n_2 q_2}{n_1 K_1} \right)^{n_1} = 0 \quad (3)$$

$$C_{2,0} - q_2 C_c - \frac{q_2}{q_1 + q_2} \left( \frac{n_1 q_1 + n_2 q_2}{n_2 K_2} \right)^{n_2} = 0 \quad (4)$$

in what subscript  $i$  ( $= 1$  or  $2$ ) represents the target compound ( $i = 1$ ) and EBC ( $i = 2$ ),  $C_{i,0}$  is the initial concentration of compound  $i$  ( $\mu\text{mol/L}$ ),  $C_c$  is adsorbent dosage (g/L),  $q_i$  is solid-phase concentration ( $\mu\text{mol/g}$ ), and  $K_i$  and  $n_i$  are single-solute Freundlich isotherm constants. As shown in equations (3) and (4), besides the adsorption parameters for the target compound ( $C_{1,0}$ ,  $K_1$  and  $1/n_1$ ), three more EBC parameters ( $C_{2,0}$ ,  $K_2$  and  $1/n_2$ ) are needed for the model prediction. To acquire the EBC parameters, a non-linear optimization algorithm that could simultaneously solve the IAST equations has been proposed (Najm et al., 1991). In the approach, three more equilibrium points at a specific initial concentration of target compound in natural water are required for defining the EBC parameters, along with single-solute parameters (Najm et al., 1991). In fact, model calibrations using two isotherms in natural water with different initial concentrations were usually used (Greene et al., 1994; Knappe et al., 1998). Najm et al. (1991) proposed that the EBC parameters ( $C_{2,0}$ ,  $K_2$  and  $1/n_2$ ) are not unique and alike modeling results may be observed by using different sets of parameters.

To evaluate the difference between model predictions and experimental data, Crittenden et al. (1999) proposed the percent sample deviation (SDEV), based on the relative error between

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